Corrosion-resistant steel sheet prodn., e.g. for the automobile industry

Publication number: DE19527515
Publication date: 1996-11-28
Inventor: GOEDICKE KLAUS (DE); METZNER CHRISTOPH (DE); BERNER KLAUS DR ING (DE); EHLERS KLAUS-DIETER (DE); STEINHOFF HARTMUT DR (DE); DUERR WILHELM DIPL PHYS DR (DE); SCHUHMACHER BERND DR (DE)
Applicant: FRAUNHOFER GES FORSCHUNG (DE); PREUSSAG STAHL AG (DE); KLOECKNER STAHL GMBH (DE); THYSSEN STAHL AG (DE); KRUPP AG HOESCH KRUPP (DE)
Classification:
- International: *C23C2/26; C23C14/16; C23C14/58;* C23C2/26; C23C14/16; C23C14/58; (IPC1-7): C23C14/16; C23C2/06; C23C14/58; C23F15/00; C25D5/36
- European: C23C2/26; C23C14/16; C23C14/58
Application number: DE19951027515 19950727
Priority number(s): DE19951027515 19950727

Also published as:
EP0756022 (A2)
EP0756022 (A3)
EP0756022 (B1)
ES2167486T (T3)

Abstract of DE19527515

A process for producing of corrosion-resistant thin steel sheet, in which a zinc-contg. coating (5) of at least 80 wt. % Zn is produced upon carbon-deficient thin steel sheet (1) by electrolytic means or immersion in a metal melt, is novel in that one or more metals (4) apart from Zn, or a metal alloy not contg. Zn is deposited by vacuum coating on the zinc-coated thin metal sheet, and then, without exposing it to an oxidising atmosphere, the sheet is heat treated in an inert gas atmosphere. The metal or metals or metal alloy not contg. zinc is produced by electron beam evaporation or magnetron sputtering. The corrosion-resistant thin steel sheet is subjected to ion bombardment or is heated to 150-400 deg C, pref. 220 deg C before the vacuum coating. The heat treatment following the vacuum coating is carried out at an inert gas pressure of 10-100 kPa, pref. 80 kPa for max. 100 seconds, pref. 0 seconds at 300-400 deg C.

Result Page

The invention concerns a procedure for the production of corrosion proof steel sheet metal on the basis of an before-improved steel sheet metal. This steel sheet metal finds in various way in the building, household appliance and automobile industry as well as in other branch of industry application.

There is well-known corrosion proof steel sheet metals on the basis of steel sheet metals, which preferably carry a coat from zinc or zinc alloys, which is applied by melting also refinement, electrolytic separating or other procedures. By the cathodic protective effect of the zinkhaltigen layer and by its barrier effect with the formation of a surface layer a good corrosion protection of the steel sheet metal is reached. These galvanized steel sheet metals become by transforming, adding, organic coating (z. B. Paint) or on other way to utensils processes. From it numerous further requirements at the customs and manufacturing properties of the Stahleinbleche.So result are economy and environmental compatibility of the production process, surface quality, transforming behavior, spot welding suitability, phosphatizing barness, kataphoretische painting barness, lacquer adhesion and corrosion protection in the unlacquered and painted condition crucial quality criteria of corrosion proof steel sheet metals apart from the demand after high corrosion protection. These demands are fulfilled however by the today available products not all time and on comprehensive way.

In the following pro and cons in the different procedures galvanized and with zinc alloy coats described before-improved steel sheet metals, whereby it is to be considered that the weighting of the individual product properties for the different consumers can be quite different. This becomes particularly clear by the example of the automobile industry, where the individual vehicle manufacturers pursue different concepts regarding the kind and quantity of the employment of before-improved steel sheet metals for the body.

Hot-dip galvanized steel sheet metals (Z) are characterised by a high corrosion protection in the unlacquered like painted Zusta and can economically and with environmentalcareful procedures be manufactured, them reach however after transforming not the surface quality of the unveredelten steel sheet metal. Concerning the spot welding barness high electrode output is not reached as with unveredelten sheet metals. Also the phosphatizing barness, the KT-Lackierbarkeit and the lacquer adhesion of hot-dip galvanized steel sheet metals cannot be regarded as optimal.

Electrolytically galvanized steel sheet metals (CPU) exhibit a better surface quality and an improved phosphatizing barness opposite hot-dip galvanized steel sheet metals (Z). The other disadvantages mentioned of Z-sheet metals cannot be avoided for CPU sheet metals. In addition it comes that the manufacturing process is by higher energy employment and the necessary disposal measures, which the wet-chemical electrolysis process draws more cost-intensive and less pollution free.

In order to adjust the lack of coats from pure zinc regarding the customs and manufacturing properties compared with unveredelten steel sheet metals, increasingly coats from zinc alloys are used. Execution variants are Galvannealed sheet metal (ZF), its coat approx. , as well as zinc nickel improved sheet metal (ZN) contains 10 mass,% iron, its coat approx. 10 . . . 12 mass,% nickel contains.

top Galvannealed sheet metal (ZF) is produced by a diffusion annealing immediately after the melting also galvanizing (to hot-dip galvanize). A very good surface quality is reached as well as compared with Z and CPU sheet metals a clearly more favorable lacquer adhesion and corrosion resistance in the painted condition. Also the electrode output exceeds that from Z and CPU sheet metals clearly.

Zinc nickel improved steel sheet metal (ZN) is manufactured by electrolytic separation of the zinc alloy on steel strip and is characterised by high corrosion resistance already in the unlacquered condition good spot welding suitability.

Both before-improved steel sheet metals, ZF and ZN, fulfill not all demands, which are made against the forming capacity. Reason for it is that the zinc alloy coats consist of inter+metallic phases and are substantially brittle therefore than coat from pure zinc. When transforming therefore microcrack arises and a far higher abrasion than when transforming steel sheet metals with coats from pure zinc. Thus also a increased wear of the material-deforming tools is connected. The selection of the available zinc alloys is process-determined strongly reduced. In addition the disposal of nickeliferous waste water represents a not insignificant cost load with the production of ZN-Überzü.

From the aforementioned one it follows that all technically introduced corrosion proof steel sheet metals exhibit certain lack with individual customs and manufacturing properties. Concluding from the professional world tries eliminating these lack and to find an optimal solution. The attempts go by, new coat for corrosion proof steel sheet metals and improved or new procedures for their production to find:
Like that it is well-known to accomplish an improved controlling of the Galvannealed process whereby the zinc coating is manufactured by evaporating in the vacuum (JP 6067690; JP 62-128168; JP 62-167870).

It is further well-known to separate on galvanically separated zinc an iron layer galvanically in order to improve the spot welding suitability (DE 19 34 081).

It is also well-known, a zinc-rich FeZn alloy with 10. . . to separate 20 mass% iron and to apply afterwards a layer from pure iron by ion plating, so that a iron-rich alloy layer or a layer from pure iron develops (JP 63-18067).

It is further well-known to apply an iron layer as surface layer on a zinc coating in order to improve the weldability (DE 19 66 807). Such coats are even and cause good painting barness and phosphatizing barness. Due to the high Eisengehaltes coat however insufficient corrosion resistance arises. So-called red rust forms.

Further it is well-known, iron-rich Fe-Zn-alloys if necessary. with alloying elements as well as further surface layers from Zn and/or ZnAl alloys to apply (JP 56-133488). From cost reasons however such layer systems are not used.

There is further a set of layers well-known for corrosion proof steel sheet metals, which are based on the fact that the corrosion protection layers made of zinc are applied by high vacuum vaporization (JP 60-56062; JP 59-83765).

Finally a multiplicity of layer systems is well-known, which contain zinc and a further, by high vacuum vaporization applied metal. So layers described from Zn with Fe (JP 1-142076; JP 1-129962), Zn with Mn (JP 1-42572; DE 44 38 608 A1), Zn with mg (JP 1-17853), Zn with aluminium (JP 1-21055; Dd 2 66 370) and further layers (JP 1-52059), Zn with mg and Fe (JP 2-305975).

All aforementioned coats for the production of corrosion proof steel sheet metals, which are manufactured completely by high vacuum vaporization, to have so far no or only very reduced technical employment found. Their production is obvious also to high costs connected. Further these layers consist predominantly of zinc alloys of relatively small ductility, so that the high abrasion specified above cannot be eliminated when transforming by such corrosion protection layers.

The invention is the basis the task to create a procedure for the production of a corrosion proof steel sheet metal which the advantages of pure zinc coatings on steel sheet metals, which is large cathodic protective effect, high ductility and comparatively small abrasion with shaping as well as simple, economical fabrication, which the condition in itself, painted by coats from zinc alloys, above all combines good spot welding suitability and good phosphatizing barness as well as good lacquer adhesion and high corrosion protection in. The procedure is not to cause high flexibility regarding the material selection and a high coating rate aufwei and at the time of its execution environmental impact.

The task is solved after the characteristics of the requirement 1. Favourable arrangements of the procedure are described in the requirements 2 to 6.

According to invention manufactured the steel sheet metal is based on the far refinement of steel sheet metals, which in more well-known point after and a proven procedure with a coat, developed technically, from zinc or a highly zinkhaltigen alloy are improved. The far refinement is reached by a surface layer, which is caused by a steered diffusion and phase education process in a limited upper, the steel sheet metal turned away range of the zinc layer. In this regard the steel sheet metal according to invention differs in principle from Galvannealed products, with which the diffusion process at the boundary surface begins between steel and zinc coating and progresses up to the outside surface of the coat.

Against the state of the art this surface layer consists of a zinc-rich alloy, whereby an education is excluded from red rust the outer surface. In not expected way is formed due to the production process zinc-rich Mischphas with or several of the metals iron, manganese, copper, magnesium, nickel, which a high, even surface quality, a good Phospatierbarkeit, a good lacquer adhesion, a good weldability with high service life of the electrodes and high corrosion protection, in particular a just as good lacquer adhesion and corrosion resistance in the painted condition as z. B. ZF-sheet metals, guarantee. The thickness of the surface layer small in the comparison to the zinc layer and their education by steered Diffusionsvorgang secure a high ductility Überzuges.Darauf are based the very small abrasion of Überzugsmaterial, proven in numerous attempts, when transforming. To emphasize is further the small thickness the surface layer of forming metal and/or. the Met or the metal craving. If the surface layer exhibits for example a thickness of 1 mu m with a zinc content of 90 mass%, so w this layer with a middle layer thickness of only 0.1 mu m in the vacuum separated and then the steered Diffusionsproze subjected. For applying this layer of metal the electron beam high rate vaporizing, preferably suitable with electron guns axial type, is particularly. Due to the high coating rate and the small thickness of the layer a speed of b run of the steel sheet metal can be achieved by the vacuum coating plant by over 200 meters per minute, how it is necessary in modern continuous steel strip refining equipments. Because of the small thickness of the layer of metal the vacuum coating can take place however in certain cases also favourably via Magnetron atomization.

In order to prepare and a high uniformity of the surface layer obtain the steered diffusion process, it is favourable, the steel sheet metal before the vacuum coating of a vacuum pretreatment by ion bombardments and/or. to subject a plasma treatment. The steel sheet metal before the vacuum coating is appropriately warmed up, vorzugswei to 220 DEG C. The thermal treatment takes place according to invention for the execution of steered diffusion and phase education process without exposition at oxidizing atmosphere. When a short time thermal treatment in direct connection was suitable to the vacuum coating during one period of 10 seconds in the temperature range between 300 DEG C and 400 DEG C proved with an inert gas pressure of 80 kPa, in order to train an even surface layer.

With a remark example the invention is more near described. Show schematically on average:

Fig. 1 a steel sheet metal provided with a zinc coating,

Fig. 2 an intermediate product after the vacuum coating,

Fig. 3 a corrosion proof steel sheet metal as final product.

In Fig. 1 is reciprocally with a zinc coating 2 provided with a thickness of 15 mu m a carbon-poor steel sheet metal 1 in well-known way by melting also refinement (hot-dip galvanizing). For far refinement this steel sheet metal 1 is degreased, cleaned and brought in over vacuum locks consisting into an electron beam volume vaporization plant, of several process chambers. The plant i on < 1 x 10< - 4> mbar evacuates. In a first process step in the first process chamber the galvanized, cleaned steel sheet metal is heated by radiant heat on 220 DEG C and in a plasma chamber an ion bombardment out law (plasma-corroded). In addition an argon low pressure gas discharge with a power density of 1,8 Wcm< works; - 2> in an impact time the steel sheet metal 1 galvanized by 1,5 seconds reciprocally on. In a following process chamber, the coating chamber, with ever one temporal-locally programs diverted electron gun vo axial type on

both sides of the galvanized steel sheet metal even 0.1 around thick layer 3 from pure iron separated (Fig. 2). In a further process chamber the steel sheet metal 1 goes through a Wärmebehandlungsstrecke at an even, temperature constantly held of (365 5) DEG C. According to the adjusted volume speed of the steel sheet metal 1 and the length of the Wärmebehandlungsstrecke the length of time for the thermal treatment amounts to 4 seconds. In this process chamber a nitrogen pressure is adjusted by 80 kPa. After one cool down-strain steps that finally improved steel sheet metal 1 over vacuum locks from the plant at air and to so-called Coils one rolls up.

Fig shows the schematic cut by according to invention manufactured the corrosion proof steel sheet metal. 3. Therein 4 represents a surface layer from a zinc-rich Zn-Fe-alloy, resulted from steered diffusion. A thickness of the surface layer is determined by methods of analysis by 1 mu m 10% with a middle sweeping stop of 8 mass%. The remaining zinc layer 5 with a remainder thickness of 13. . . 14 mu m is iron-free in the context of the analysis accuracy.

The corrosion proof steel sheet metal exhibits also with high grades of deformation a very small abrasion when transforming, that from hot-dip galvanized sheet metals (Z) corresponds. Roughness and uniformity of the surfaces as well as Punktschweissbarke phosphatizing barness, lacquer adhesion and corrosion behavior after order for lacquer approximate against it the characteristics of ZF (Galvannealed sheet metal) or exceed these characteristics. The manufacturing process can be accomplished following a melting also refinement and with same volume speed. It is high productive and besides free thereby from polluting waste products.